Use of Cavity Ringdown Spectroscopy (CRDS) to Deliver Nitrate Radicals for Indoor Surface Chemistry

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1 Introduction

Cleaning and room deodorizing are common activities that can introduce a number of volatile organic compounds into the indoor environment. Application of these chemicals leads to diffuse gas-phase "clouds" and/or adsorption to surfaces also present indoors. These compounds can then react both in the gas phase and/or on surfaces with indoor oxidants such as the nitrate radical (NO_3•) resulting in the formation of new chemical species that can be emitted into the indoor environment and affect occupant exposure.

In order to simulate real world concentrations (1 – 58 ppt) of nitrate radicals that are expected to be indoors as modelled by Sarwar et al. (Sarwar, 2002) and measured Nojgaard (Nojgaard, 2010), a sensitive absorption technique such as cavity ringdown spectroscopy (CRDS) may be employed. CRDS can be used to deliver accurate NO_3• concentrations for gas or surface-phase experiments. Several CRDS measurements of NO_3• have been made in the atmospheric environment with instruments having detection limits in the sub ppt range (Ayers, 2005, Brown, 2005).

To investigate the reactions of the nitrate radical with α-terpineol on a silanized glass surface, a custom CRDS system was developed. This platform will describe the instrument, show NO_3• calibration curves from this system, and discuss the preliminary results from α-terpineol/ NO_3•/silanized glass reactions.

2 Materials/Methods

Surface chemistry experiments were carried using the previously developed FLEC Automation and Control System (FACS) (Flemmer, 2007). Briefly, the FACS is composed of three stages: air purification, air humidification, and reactant injection and delivery stage.

The FACS was coupled to the CRDS system that was built in-house. The CRDS system consists of a heated glass flow tube for mixing ozone and NO_2 and the absorption cavity. The cavity is made of a 1.5 in. I.D. stainless steel tube with 1 in. I.D. Teflon tube inserted. At the ends of the tube are two highly reflective mirrors (99.9995% at 662 nm, Advanced Thin Films, Boulder, CO). A diode laser (Power Technology Inc., Alexander, AR) with a wavelength at 662 ± 0.2 nm was used to determine nitrate radical concentration using its absorption coefficient ($\sigma_{662,\ 80^oC} = 1.7x10^{-17}$ cm^2 $molecule^{-1}$) (Sander, 1986).

α-terpineol was applied to a 10 in. x 10 in. x 1/8 in. silanized glass surface using a previously described sprayer (Ham, 2008). Once a-terpineol was applied to the glass surface, the glass was placed in a 24 L Teflon coated chamber and NO_3• was introduced to the surface.

Emissions from the α-terpineol/ NO_3• surface reactions (FACS) were collected in a 100 mL glass impinger immersed in a thermostated water bath at 0 ± 0.5 ^oC controlled by an immersion chiller (EK45, Fisher Scientific, Pittsburgh, PA) and connected to the output of the FLEC using 0.64 cm O.D. Teflon tubing. To the impinger, 14.7 mL of HPLC grade methanol was added. Output air from the FLEC at 300 mL min^{-1} was bubbled through the impinger for 12 hours.

At the end of the 12 hour sampling period, the solution left in the impinger (~ 4 mL) was divided into two 4 mL amber vials. The first

vial (labeled 1A) was filled with 2.0 mL of solution from impinger. The remaining solution (~1.5 – 2 mL) was placed in the second vial (vial 1B). To identify reaction products (i.e., aldehydes, ketones, and dicarbonyls), 200 µL of PFBHA (20 mM in ACN) was added to the 1A vials. These vials were then left overnight to allow for the reaction to go to completion. No PFBHA was added to the 1B vials.

After reaction completion, the 1A vials were blown to complete dryness using UHP N_2 then reconstituted in 100 µL of methanol. The 1B vials were unaltered and injected as pure samples. All samples were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in the electron impact (EI) mode.

3 Results

Using the custom CRDS system an empty cavity (N_2 only) ringdown time of 84.0 µs was achieved. In the initial experiments O_3 (200 ppb) and NO_2 (250 ppb) were mixed in the heated tube at 300 mL min^{-1} at 600 Torr which gave a residence time of ~12 sec. The measured ringdown time at these concentrations of O_3 and NO_2 was 76.4 µs which translated to a NO_3• concentrations of 83 ppt. Calibration curves were developed using this setup by varying the O_3 and NO_2 concentrations in the cavity.

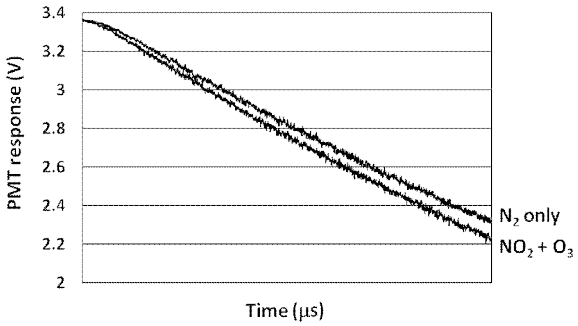

Figure 1: Ringdown signal from N_2 only and Addition of O_3 and NO_2 in cavity.

4 Conclusions

This data shows that the CRDS system can be used to measure NO_3• concentrations that are expected to exist indoors.

A-terpineol reactions with the nitrate radical have been studied in the gas-phase, but no data exists for its reaction on indoor surfaces. These experiments are currently being done; however preliminary results show the formation of organic nitrate species generated from surface reactions on silanized glass. Identification of reaction products results will be discussed after further confirmation.

5 References

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